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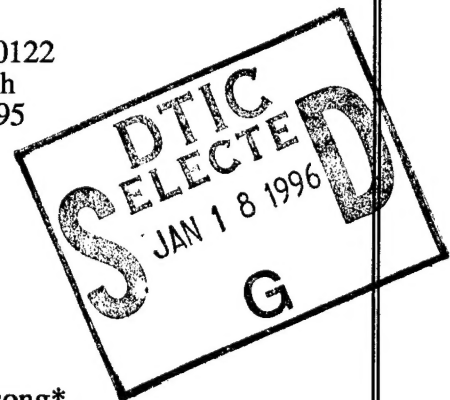
Selected Energy Epitaxial Deposition and Low Energy
Electron Microscopy of AlN, GaN and SiC Thin Films

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13. ABSTRACT (Maximum 200 words)

As-received wafers of n- and p-type 6H-SiC(0001) were etched via gaseous HCl in H_2 at 1350°C at NASA-Lewis to remove cutting and polishing scratches from the surface; however, etch pits were created. GaN films have been deposited on Si(100) and Al_2O_3(0001) substrates using triethylgallium and NH_3 seeded into highly expanded He gas streams. A two-step deposition process that repeatedly resulted in continuous crystalline GaN films has been developed. The microstructure and composition of the resultant films were characterized by SEM, RHEED and AES and film character correlated to deposition conditions. Assembly of a new dual seeded beam deposition and film analysis facility is underway. In addition, the main chamber of a dual Colutron ion-beam deposition system for the deposition of high-quality SiC and GaN films is nearing completion. Ion sources have been assembled and leak-tested. Preliminary results on the characterization of a seeded supersonic molecular beam source are presented. A room temperature beam of 10% NH_3 with a source pressure of 25 kTorr and a 25 μm nozzle produces NH_3 molecules with mean energies of 0.264 eV and an energy spread of 0.068 eV. Modifications to the existing system are discussed.

14. SUBJECT TERMS

6H-SiC, HCl, etching, GaN, films, triethylgallium, NH_3, seeded beams, microstructure, Colutron, ion-beam deposition, supersonic molecular beam

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Table of Contents

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I. Introduction

The realized and potential electronic applications of AlN, GaN and SiC are well known. Moreover, a continuous range of solid solutions and pseudomorphic heterostructures of controlled periodicities and tunable bandgaps from 2.3 eV (3C-SiC) to 6.3 eV (AlN) have been produced at North Carolina State University (NCSU) and elsewhere in the GaN-AlN and AlN-SiC systems. The wide bandgaps of these materials and their strong atomic bonding have allowed the fabrication of high-power, high-frequency and high-temperature devices. However, the high vapor pressures of N and Si in the nitrides and SiC, respectively, force the use of low deposition temperatures with resultant inefficient chemisorption and reduced surface diffusion rates. The use of these low temperatures also increases the probability of the uncontrolled introduction of impurities as well as point, line and planar defects which are likely to be electrically active. An effective method must be found to routinely produce intrinsic epitaxial films of AlN, GaN and SiC having low defect densities.

Recently, Ceyer [1, 2] has demonstrated that the barrier to dissociative chemisorption of a reactant upon collision with a surface can be overcome by the translational energy of the incident molecule. Ceyer's explanation for this process is based upon a potential energy diagram (Fig. 1) similar to that given by classical transition-state theory (or activated-complex theory) in chemical kinetics. The dotted and dashed lines in Fig. 1 show, respectively, the potential wells for molecular physisorption and dissociative chemisorption onto the surface. In general, there will be an energy barrier to overcome for the atoms of the physisorbed molecule to dissociate and chemically bond to the surface. Depending upon the equilibrium positions and well depths of the physisorbed and chemisorbed states, the energy of the transition state E^* can be less than zero or greater than zero. In the former case, the reaction proceeds spontaneously. In the latter case, the molecule will never proceed from the physisorbed state (the precursor state) to the chemisorbed state unless an additional source of energy can be drawn upon to surmount the barrier. This energy can only come from either (1) the thermal energy of the surface, (2) stored internal energy (rotational and vibrational) of the molecule, or (3) the incident translational kinetic energy of the molecule. Conversion of translational kinetic energy into the required potential energy is the most efficient of these processes. Moreover, by adjusting the kinetic energy, E_i, of the incoming molecule, it is possible to turn off the reaction $(E_i < E^*)$, to tailor the reaction to just proceed $(E_i = E^*)$, or to set the amount of excess energy to be released $(E_i > E^*)$. The thrust of the present research is to employ these attributes of the beam translational energy to tune the reaction chemistry for wide bandgap semiconductor epitaxial growth.

The transition state, E^*, is essentially the activation energy for dissociation and chemisorption of the incident molecules. Its exact magnitude is unknown, but is most certainly
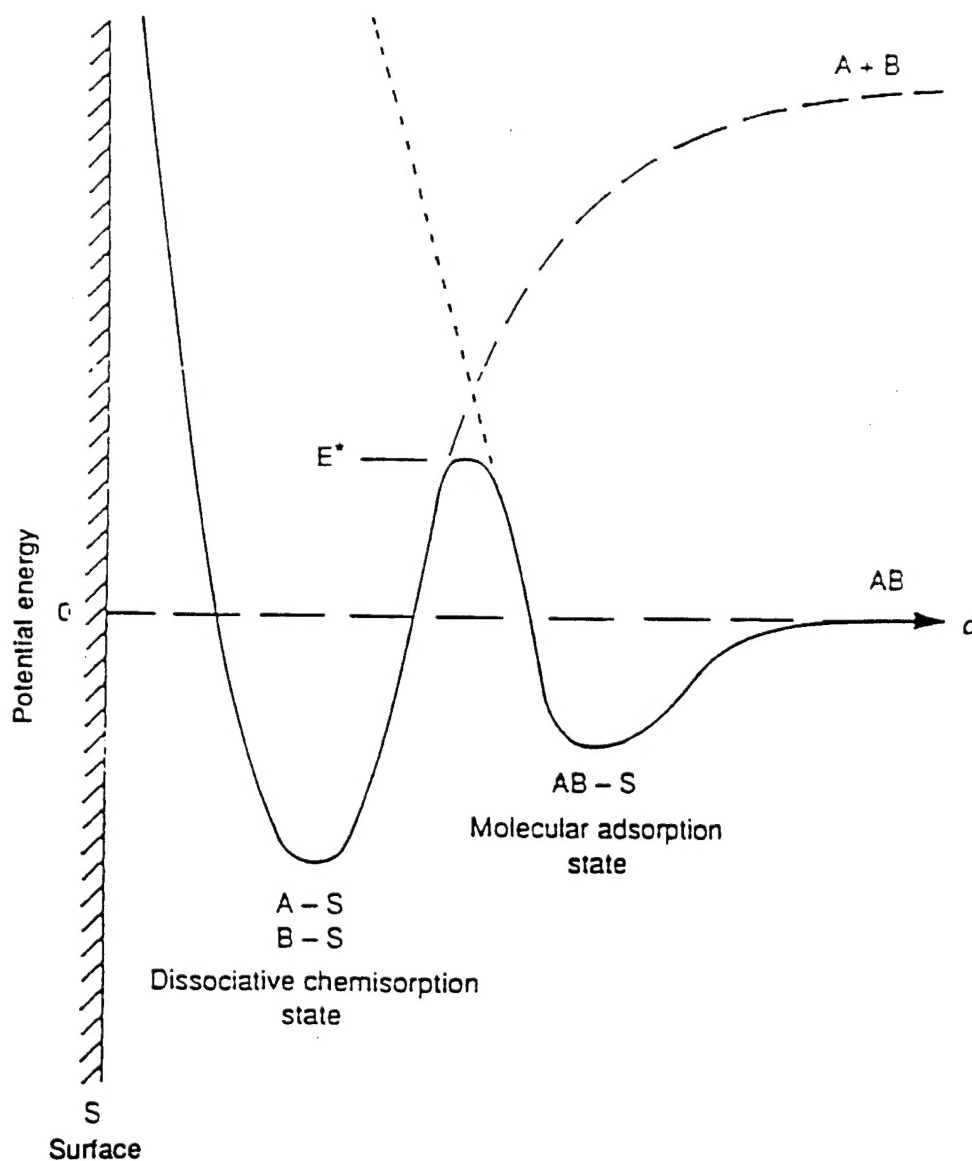
Figure 1.   Schematic potential energy diagram of an activated surface reaction involving a molecularly physisorbed precursor state [from Ref. 1].

lower than the dissociation energy of the free molecule. It does not necessarily follow, however, that any kinetic energy above E^* will promote high-quality epitaxial growth of GaN. One must take into consideration another energy threshold, E_d, beyond which the kinetic energy of the incident flux will cause damage to the epitaxial film being synthesized. A typical E_d threshold value is approximately five times the bandgap of the crystal and in the case of GaN, $E_d \approx 18$ eV.

From the above consideration, it is clear that the key to high quality epitaxial growth is to be able to tune the energy of the incoming flux species over a range of energies defined by the window between E^* and E_d. Since the window is quite restrictive, i.e. 1-20 eV, it is essential

2

that the energy spread of the flux species must be small, i.e. the flux species should ideally be monoenergetic. To this end, we employ Selected Energy Epitaxial Deposition (SEED) systems for the growth of AlN, GaN and SiC wide bandgap semiconductors. The SEED systems are of two types: (1) a seeded-beam supersonic free-jet (SSJ) and (2) a dual ion-beam Colutron. Both these SEED systems have the desirable property of a narrow energy spread of ≤ 1 eV.

Epitaxial growth using the seeded-beam SSJ involves a close collaboration between investigators at NCSU and Arizona State University (ASU). At ASU, the SSJ is interfaced directly into a low-energy electron microscope (LEEM) for the conduct of *in situ* studies of the nucleation and growth of epitaxial layers; while at NCSU, the SSJ systems are used to grow device-quality AlN, GaN and SiC for real applications. Exchanges in personnel (students) and information between the two groups ensures the achievement of desired results. The additional thin film growth experiments using dual-beam Colutrons and the theoretical studies referred to in this report are primarily conducted at ASU.

The research conducted in this reporting period and described in the following sections has been concerned with (1) removal via high temperature etching of as-received cut and polished wafers of 6H-SiC(0001), (2) deposition of GaN films using a two-step, NH_3-seeded, highly expanded He gas stream and triethylgallium, and (3) the assembly of a new III-V nitride and SiC deposition system involving seeded supersonic beams and dual Colutron ion-beams. The following individual sections detail the procedures, results, discussions of these results, conclusions and plans for future research. Each subsection is self-contained with its own figures, tables and references.

1. S. T. Ceyer, Langmuir **6**, 82 (1990).
2. S. T. Ceyer, Science **249**, 133 (1990).

3

II. Surface Microstructure of 6H-SiC(0001) Substrates for Nitride Film Growth

A. Introduction

Various etching procedures described in previous reports have not led to the desired result of minimizing the surface defects in commercially available SiC. In order to conduct meaningful growth studies by LEEM, these defects must be minimized. We have continued to explore other techniques to accomplish this goal.

B. NASA Lewis Research Center Process

As pointed out in our previous report of September, 1995, two test crystals were sent to NASA Lewis Research Center which uses a high temperature surface preparation procedure. The procedure is a pregrowth etch of the SiC substrate by gaseous HCl in H_2 at a temperature ~ 1350°C [1]. The authors stated that this etch significantly reduces defects caused by the cutting and polishing of wafers; and our results seem to support this fact. The samples sent to NASA Lewis were a p- and n-type 6H-SiC(0001) purchased from Cree Research. Silicon terminated sides were etched and both samples were done at the same time. Figure 1(a) shows the surface morphology of the p-type sample before the etch and Fig. 1(b) is the morphology after the etch. Figure 2(a) shows the surface morphology of the n-type sample before the etch and Fig. 2(b) is the morphology after the etch. It is important to note that the scratches present before the etch have disappeared in both samples after the etch. Both samples have etch pits, but the area between the etch pits in the n-type sample, Fig. 2(b), is particularly clean. The p-type surface in Fig. 1(b) contains small areas with bright contrast distributed randomly and we are not certain at this point about the nature of the surface microstructure between the etch pits.
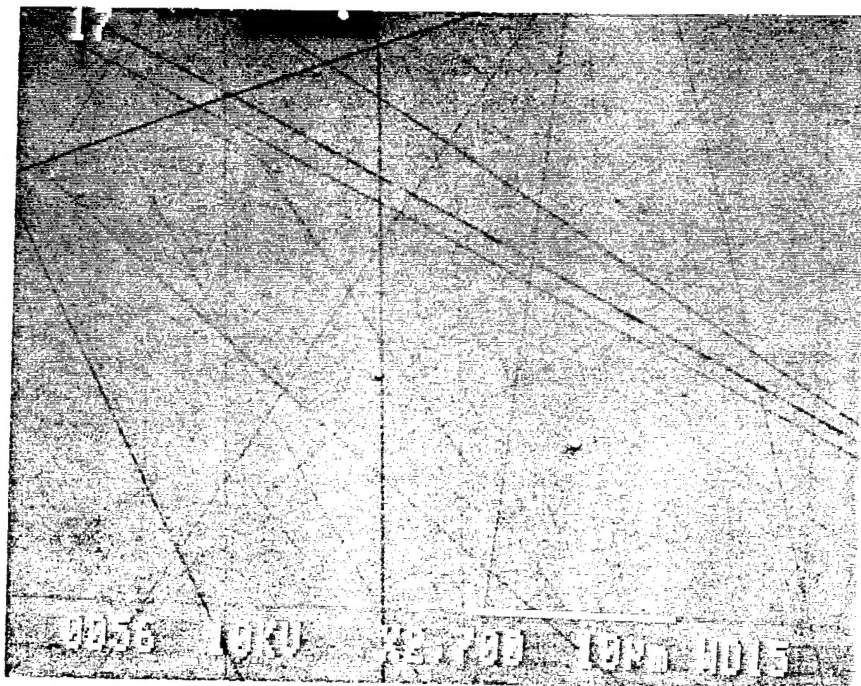
These samples will be examined in the LEEM to ascertain their suitability in the future experiments. Additional samples will be sent to NASA Lewis for further etch studies.
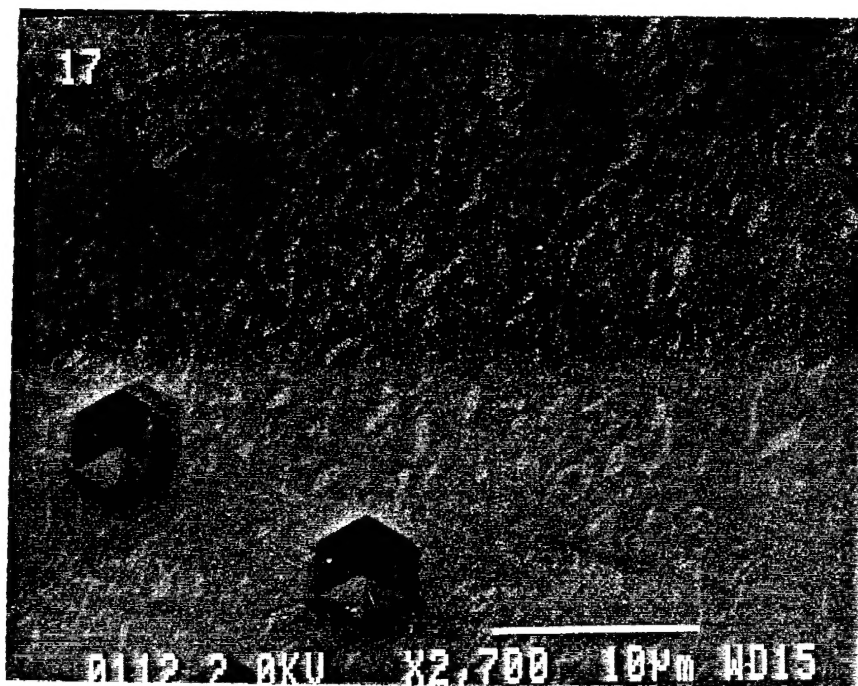
C. Conclusions

The NASA Lewis etch process appears to have removed the scratches, but pending future LEEM investigations, we do not have a definite conclusion on the surface morphology and microstructure.

D. References

1. David J. Larkin and J. Anthony Powell, U.S. Patent # 5,363,800, Nov. 15, 1994.
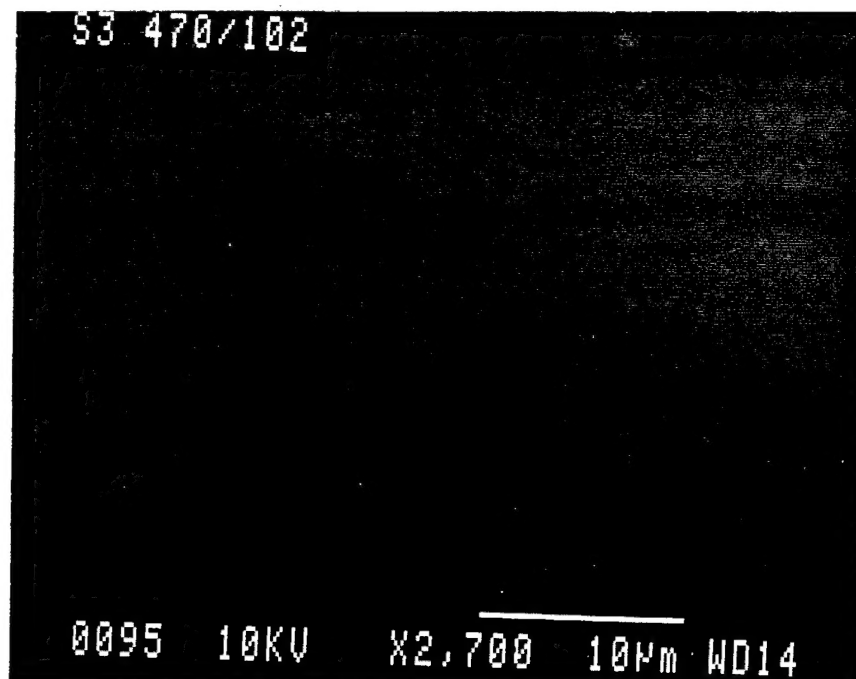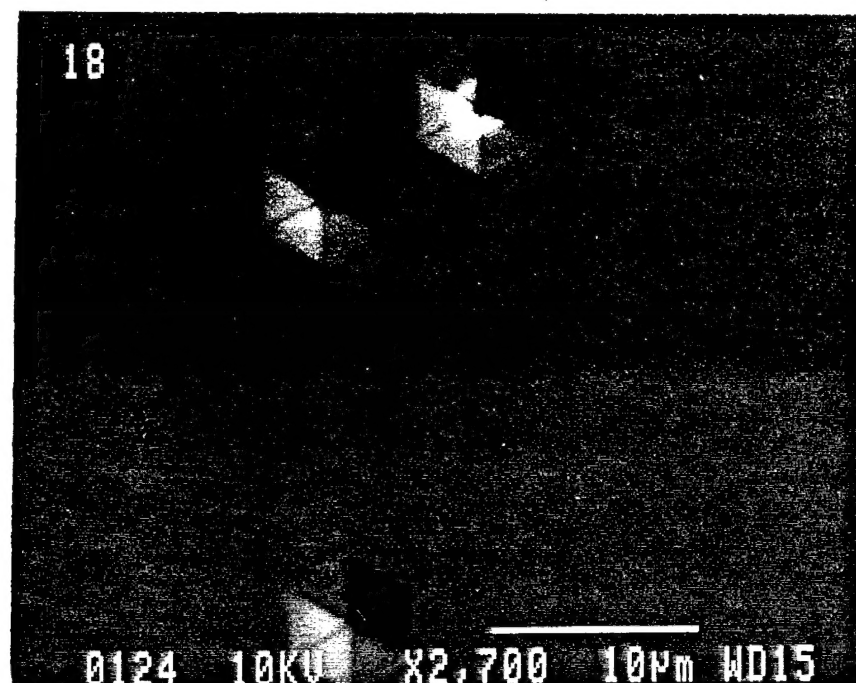
(a)

(b)

Figure 1. (a) The surface morphology of the p-type sample before the etch and (b) the surface morphology of the p-type sample after the etch.

5

(a)

(b)

Figure 2.   (a) The surface morphology of the n-type sample before the etch and (b) the surface morphology of the n-type sample after the etch.

6

III. Selected Energy Epitaxial Deposition and Low Energy Electron Diffraction of GaN and SiC Thin Films

A. Introduction

Gallium nitride thin films are of considerable interest in the development of blue light emitting diodes (LEDs) for panchromatic solid state displays. In addition to LEDs, GaN may be used for the fabrication of blue solid state lasers which would facilitate the achievement of greater data density in optical transmissions and optical storage media. Chemical vapor deposition (CVD) is the most popular technique currently employed to grow GaN films [1]. However, this method requires very high deposition temperatures that complicate device design fabrication processes. A reduction in the required deposition temperature is highly desirable. In many thin film deposition processes, activation energy barriers must be overcome in order to grow a film. Typically, this energy is supplied by the thermal energy of the substrate. Alternatively, several novel approaches such as plasma discharges [2,3] have been examined as a means of supplementing this thermal energy and assisting in overcoming the activation energy barriers to GaN film deposition via the generation of activated precursors. Unfortunately, plasma processes may damage the substrate or device structures due to ionization effects and ion bombardment.

An interesting alternative to plasma processing is the employment of seeded highly expanded gas streams. Heavy reactant molecules seeded into a majority stream of light molecules are swept along at superthermal velocities acquiring a substantial amount of kinetic energy, up to several eV, that can aid in driving subsequent surface reactions. Also, the velocity spread of the seeded molecules is inversely related to the stagnation pressure, permitting the formation of a very monoenergetic molecular beam. With the ability to generate a neutral beam of a well-determined, selective energy, surface reaction pathways can be studied in detail.

This report details the recent developments in the deposition of GaN films using seeded highly expanded beam sources. In this reporting period, the assembly of a new dual skimmed, differentially pumped, seeded beam deposition and film characterization facility has progressed significantly. The results of the current research and the status of the assembly of the new instrument are presented.

B. Experimental Procedure

Deposition System. Films were deposited in a free-standing supersonic beam reactor that was described in detail in the previous report (Sept., 1995) and which has been reconfigured to generate two free jets as depicted in Fig. 1. The NH_3 nozzle is surrounded by a heating coil and is capable of achieving temperatures of up to 600°C while the TEGa nozzle is unheated. Research grade He was used as a carrier while high purity NH_3 was further purified using a Nanochem® activated resin bed purifier. Samples were mounted onto stainless steel travelers

and introduced into the reactor through a loadlock. The travelers were mounted to a stainless steel housing that was heated by a tungsten halogen lamp giving substrate temperatures of up to 650°C. Typical operating conditions are summarized in Table I.
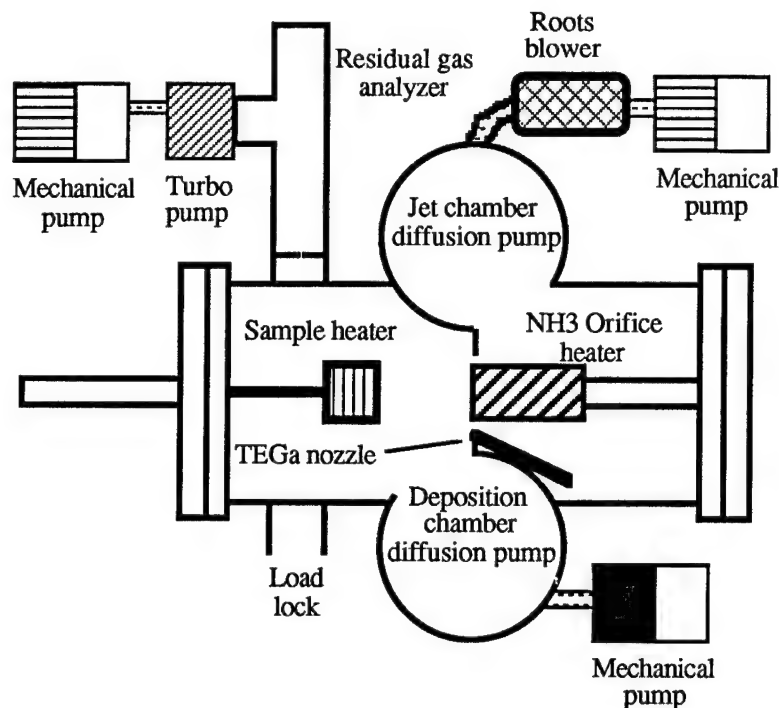

Figure 1.   Supersonic jet deposition system configured with dual free jets.

Table I. Typical Experimental Conditions/System Capabilities

System Parameter	Value
Base vacuum	8×10^{-7} Torr
Pressure during deposition	5×10^{-4} Torr
NH_3 seeding percentage	5% volume
NH_3 jet stagnation pressure	800 Torr
NH_3/He flow rates during deposition	12/240 sccm
NH_3 orifice diameter	150 μm
NH_3 orifice temperature	550°C
TEGa bubbler temperatures	-10°C
TEGa stagnation pressure	860 Torr
TEGa carrier	40 sccm He
TEGa orifice diameter	20 μm
TEGa delivery rate	0.034 sccm
NH_3:TEGa ratio	354:1
Substrate temperature	600°C

Sample Cleaning/Preparation. Al_2O_3 (0001) samples were prepared in a three-step cleaning process. First, samples were degreased via immersion for 10 minutes in a trichloroethylene containing ultrasonic bath. Next, samples were placed for 15 minutes in an 80°C acid bath containing a 50:50 mixture of H_3PO_4 and H_2SO_4. Finally, the samples were immersed in a 10% HF solution for 5 minutes. Si(100) samples were firstly immersed in a 10% HF solution for 5 minutes and subsequently exposed to an ultraviolet light: air oxidation step after which the samples were immersed in a separate 10% HF solution for 5 minutes. Both Al_2O_3(0001) and Si(100) substrates were blown dry with LN_2 boil-off immediately before mounting on travelers and installation into the reactor.

Auger Analysis. For Auger electron spectroscopy, samples were removed from the supersonic beam deposition reactor and transferred in air to a 10^{-10} Torr base pressure ultrahigh vacuum analysis system. The analysis chamber contains a Physical Electronics 10-155 cylindrical-Auger Electron optics detector with a coaxial electron gun operated by a Physical Electronics 11-010 electron gun controller. The Auger optics were supported by a Physical Electronics 32-100 electron multiplier module. Samples were Ar ion milled *in-situ* prior to Auger examination. Auger measurements were performed with a primary electron energy of 3 keV and data was collected for 10 ms at each 1 eV scanning step for 15 iterations.

Reflection High Energy Electron Diffraction. Electron diffraction analysis of deposited films also required an in air transfer to a separate analysis chamber housing a Physical Electronics electron gun operated at up to 10 keV by a 20-330 analog HEED gun controller. The electron source was 12" from the sample center and the screen was also 12" from the sample center. Diffraction patterns were taken at a 10 keV beam voltage.

Scanning Electron Microscopy. A JEOL 6400 field emission scanning electron microscope (SEM) operated with a 5 keV primary beam was used for the SEM images in this report. The samples were cleaved immediately before installation in the SEM for cross sectional images.

C. Results and Discussion

Single Step Deposition. A series of experiments was performed to study the effects of the NH_3:TEGa ratio on the properties of resulting films when using two free jet sources. This is an extension of a similar series reported in the previous report (Sept., 1995). By varying only the TEGa bubbler temperature while holding all flow rates and pressures constant, it was possible to explore this ratio effect without the added complication of gas flow patter changes. The variation in the NH_3:TEGa ratio with changes in bubbler temperature under the selected conditions are tabulated in Table II. Three samples were prepared and examined via SEM and Auger chemical spectroscopy. Figure 2 displays the Auger spectra collected from the four samples. A clear trend of decreasing N concentration with decreasing NH_3:TEGa supply ratio is evident.

Table II. Bubbler Temperature and NH_3:TEGa Ratio for Deposition Studies

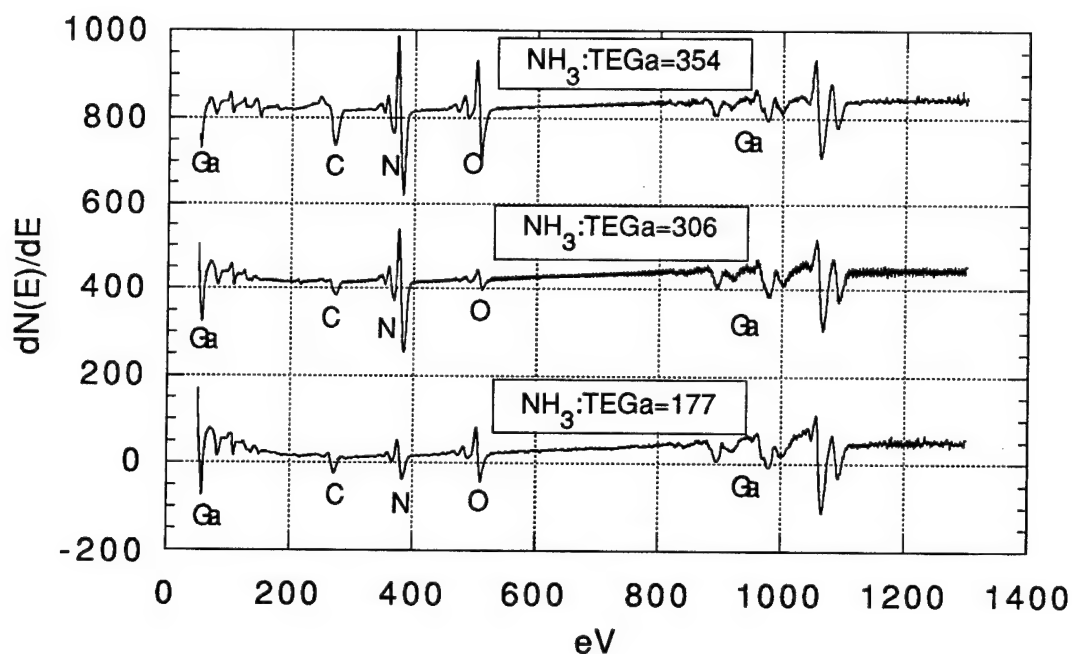| Run Number	Bubbler Temp.	NH_3:TEGa Ratio
1	0°C	177
2	-8°C	306
3	-10°C	354

Figure 2.　　Auger electron spectra of films deposited at varying NH_3:TEGa supply ratios.

An SEM image of a GaN film deposited on an $Al_2O_3(0001)$ substrate under a NH_3:TEGa supply ratio of 177 is presented in Fig. 3. Spherical particles visible on this surface are hypothesized to be globules of Ga surrounded by a skin of GaN. Meanwhile, a GaN film deposited under a NH_3:TEGa supply ratio of 354 is presented in Fig. 4. The very bright regions are the underlying Al_2O_3 substrate that has not been completely covered even after one hour of deposition.

These two cases represent two extremes encountered when deposition is performed with low and high NH_3:TEGa ratios, respectively. Although higher NH_3:TEGa ratios produce films closer to stoichiometry, the nucleation and growth of GaN under these conditions occurs very slowly. From these results, it was inferred that the initial nucleation of a GaN on the substrate is very difficult to accomplish at high NH_3:TEGa ratios. To further expand on this effect, an
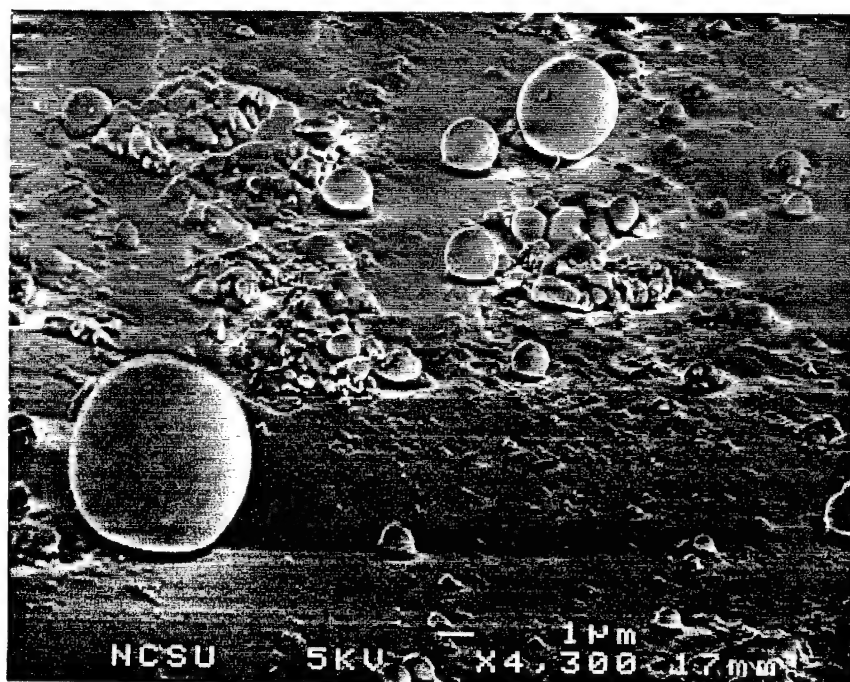
Figure 3.   GaN film deposited on an $AL_2O_3(0001)$ substrate under a NH_3:TEGa supply ratio of 177.
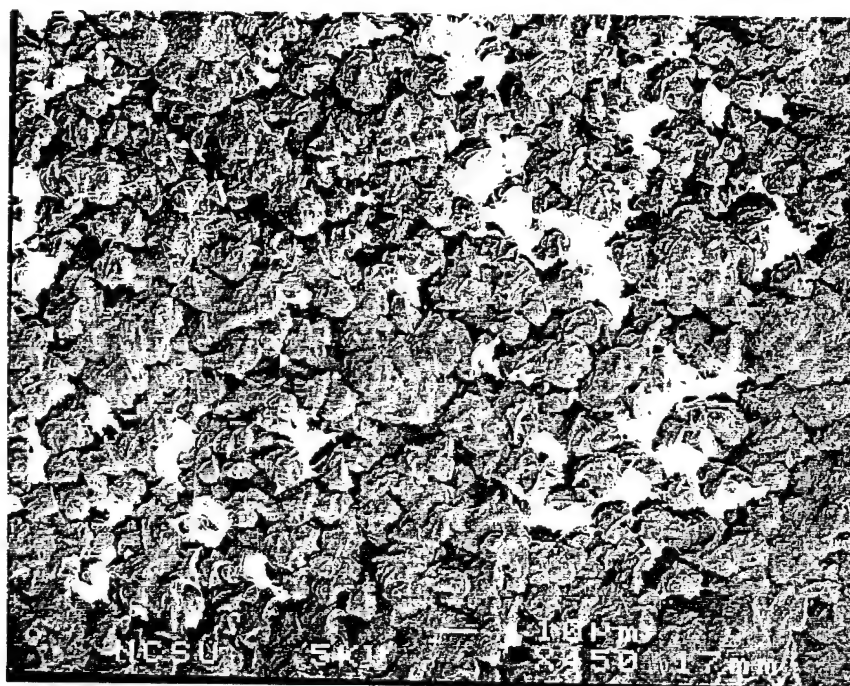

Figure 4.   GaN film deposited on an $AL_2O_3(0001)$ substrate under an NH_3:TEGa supply ratio of 354.

additional experimental deposition run was performed in which the NH_3:TEGa ratio was increased to 617. To achieve such a high value, it was necessary restrict the gas flow between the TEGa bubbler outlet and the TEGa nozzle using a needle valve. This valve was set to maintain a TEGa bubbler pressure of 750 Torr at 20 sccm He carrier flow while the TEGa nozzle operated at a 400 Torr stagnation pressure. Figure 5 is an inclined view of the resulting GaN film on a Si(100) substrate. There was very little deposition on the Al_2O_3(0001) substrate run under the same conditions. Rounded hills of GaN are visible in Fig. 5 while these features are seen in Fig. 6, a cross sectional view, to originate at the Si(100) surface. Little evidence is visible of secondary nucleation during the majority of this five hour growth run.
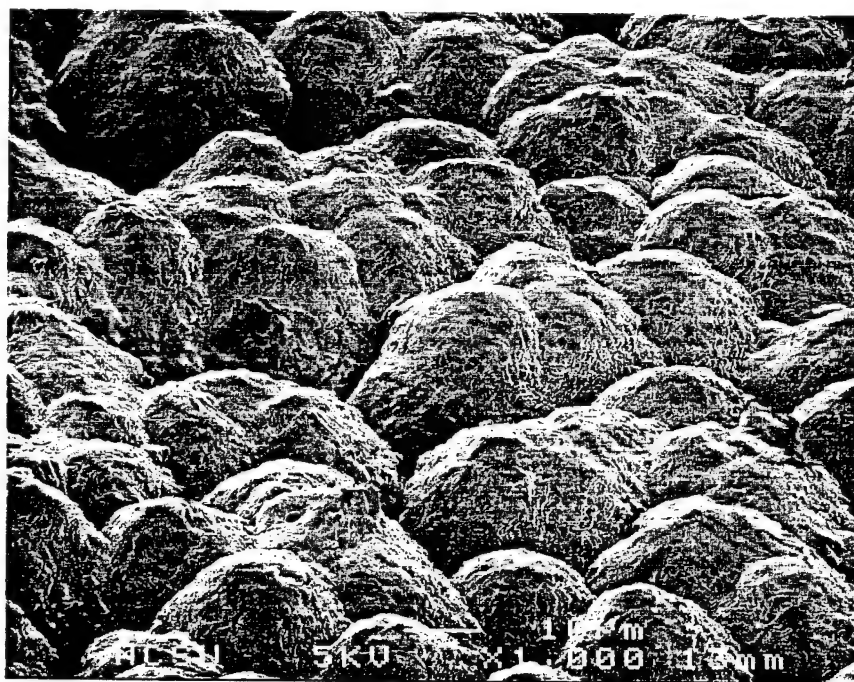

Figure 5.   GaN film deposited on a Si(100) substrate under an NH_3:TEGa supply ratio of 617.

These results indicated the desirability of separating the deposition of GaN films using seeded supersonic free jet sources into two stages: a nucleation or induction stage and a growth stage. The nucleation stage should occur under the relatively TEGa-rich conditions that are inferred to favor the formation of stable nuclei. Meanwhile, the growth stage should be performed under the relatively NH_3-rich conditions the are more favorable to the formation of stoichiometric GaN films.

Dual Step Deposition. One possible mechanism available to change the NH_3:TEGa ratio during a deposition run was to change the bubbler pressure and, hence, the TEGa concentration and flow rate. This approach was dismissed because of the possibility that
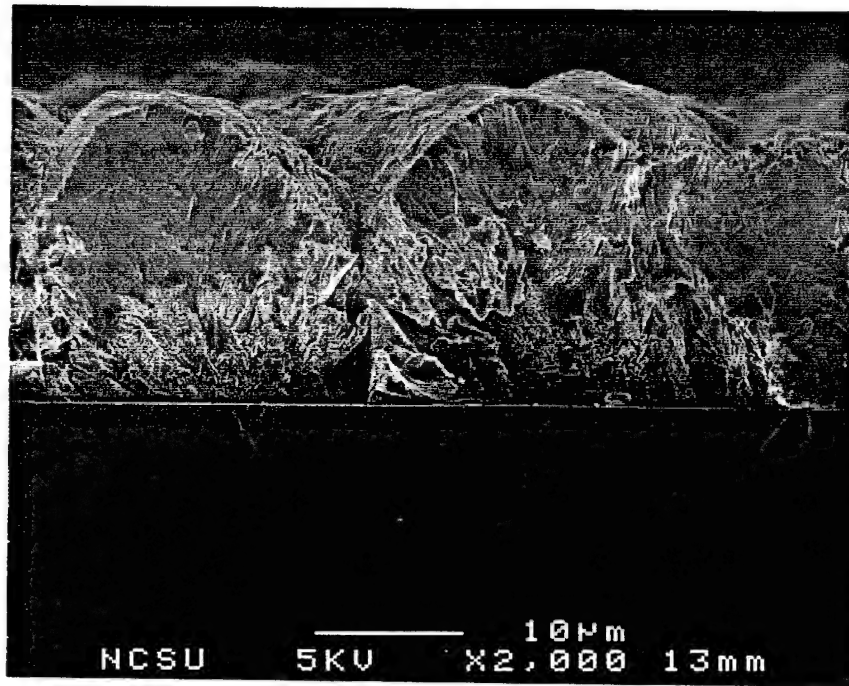
Figure 6.   GaN film deposited on a Si(100) substrate under an NH_3:TEGa supply ratio of 617.

changing gas flow rates or orifice pressures could alter the gas dynamics during deposition. The alternative technique of altering the substrate temperature was selected due to the relative simplicity of this approach. Although changing the temperature of the substrate does not alter the NH_3:TEGa supply ratio, it can alter the N precursor: Ga precursor ratio on the surface. The residence time (τ_R) of an adsorbed species is inversely related to temperature [4] as shown below in Eq. 1 and increasing the residence time should increase surface density (n_A) by Eq. 2 [4]. In these equations, E_a is the bonding energy of species a, τ_0 is a characteristic time factor typically approximated by the lattice vibration time of $\approx 10^{-13}$ seconds and R is the incident flux of species a. In accepting this technique as a way to alter the N precursor: Ga precursor surface ratio it is assumed that the E_a for Ga precursors is $\gg E_a$ for the N precursors.

$$\tau_R = \tau_0 exp\left(\frac{E_a}{kT}\right), \tag{1}$$

$$n_A = R\tau_R. \tag{2}$$

To develop a two-step process, a series of experiments were performed as listed in Table III. In all of these deposition runs, the sample was first heated up to an intermediate temperature (T1) and the TEGa flow was initiated. The sample was then held at T1 for M minutes before ramping to 600°C in $\approx$ 10 minutes. To stop deposition, the TEGa flow was

13

terminated and the sample cooled under the NH3 jet until the substrate temperature decreased to below 200°C. The sample was then transferred to the Auger analysis system, Ar ion milled for 10 minutes and the Auger spectra in Fig. 6 were collected as described before.

Table III. Experimental Runs to Study Two-step Deposition Process.
NH3:TEGa ratio = 354

Run Number	T1	M
1	500°C	10
2	550°C	20
3	550°C	5
4	550°C	1
5	550°C	0

The Auger spectra in Fig. 7 have all been normalized to the same Ga peak intensities. By comparing the spectra, the films deposited after pretreatment s #4 and #5 had the highest N:Ga ratios and, thus, were the films that were closest to stoichiometry.

GaN films deposited under the conditions employed for Run #5 were optically transparent with a red-gold color. The films also contained a very large number of cracks which are attributed to the large lattice and thermal expansion mismatches (33% and 25%, respectively) [5] between the GaN film and the Al_2O_3 substrate. This film was further examined using SEM and RHEED.

The inclined surface view in Fig. 8 pictures a region where part of the GaN film has delaminated from the substrate and is missing while nearby, the film buckles upward along a crack. This cracking and buckling is better pictured in Fig. 9 where a large section of the film has separated and has curved away from the substrate. Figure 10 is a cross sectional image of the GaN film and faceting is visible along the cleavage plane. RHEED diffraction patterns for this film are presented in Fig. 11 and are consistent with a polycrystalline film exhibiting a large degree of preferred crystallographic orientation. The degree of preferred orientation observed in this film in addition to the cracking are very encouraging results. It may prove possible with continued refinement to develop a process to deposit monocrystalline GaN films on $Al_2O_3(0001)$ or other suitable substrates such as 4H or 6H SiC(0001) substrates at a temperature as low as 600°C at deposition rates in the μm/hr range.

Seeding in Ar Free Jets. Although there are several indications in the research to this point that seeding NH3 and TEGa in He beams enhances film deposition character, a series of experiments were initiated to validate this point. The seeding effect has been expected to be
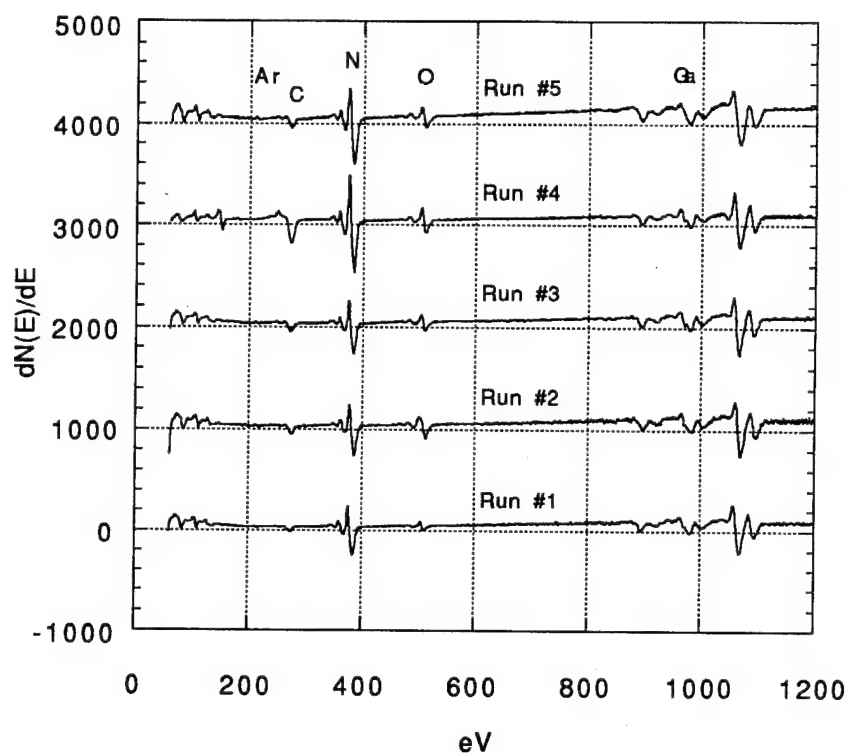
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Figure 7.   Auger spectra of samples prepared under conditions in Table III.
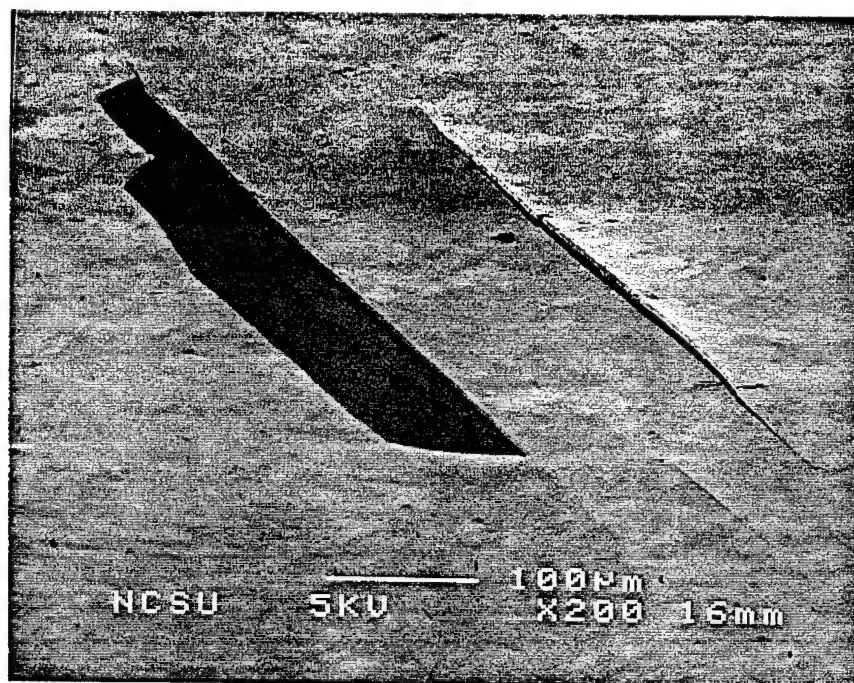

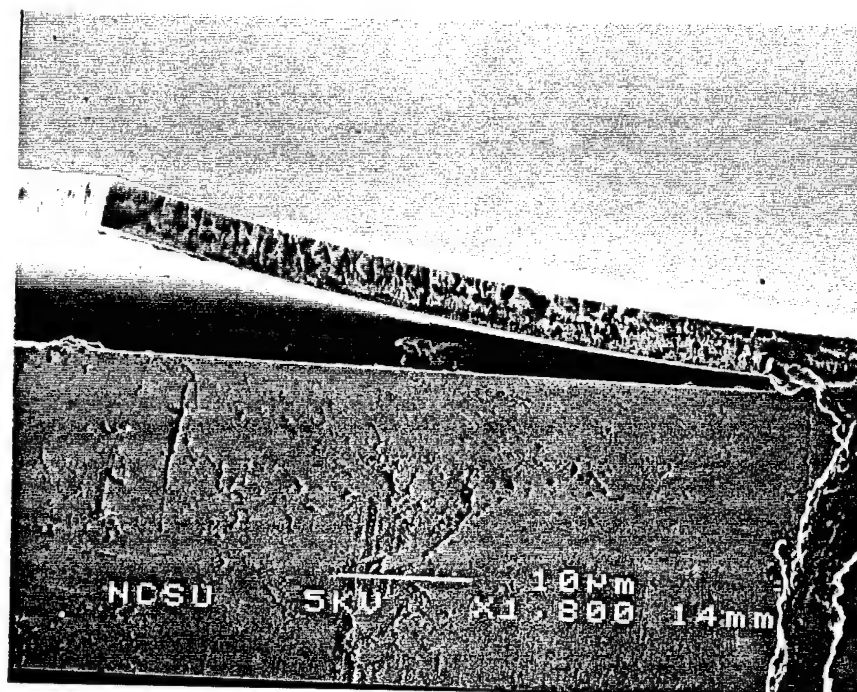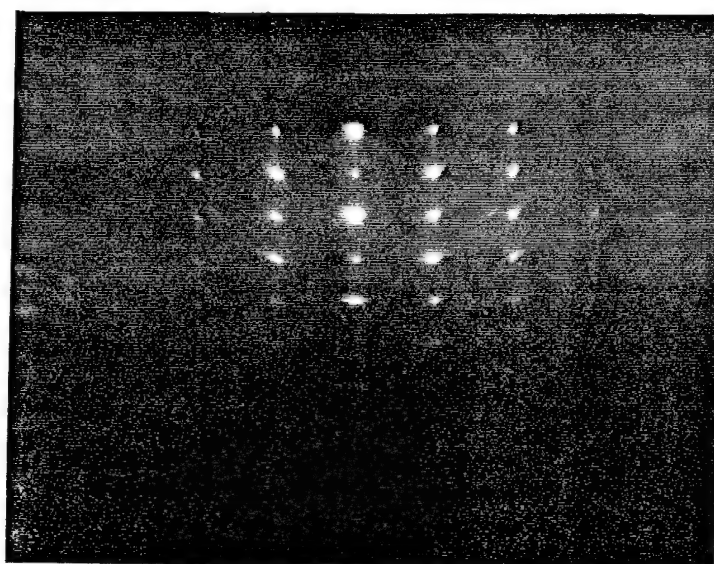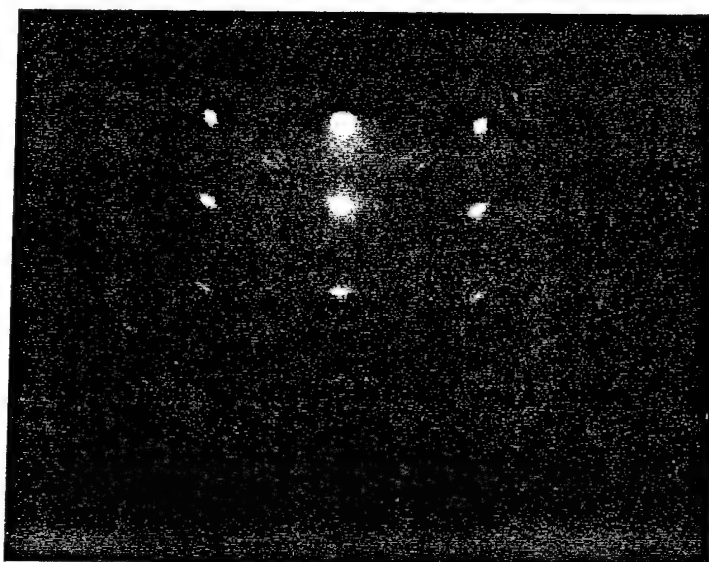Figure 8.   Delamination and cracking in GaN film on Al$_2$O$_3$ substrate.

Figure 9.   Region of GaN film curling back from Al$_2$O$_3$ substrate.

Figure 10.   Cross sectional view of GaN film exhibiting faceting.

16

(2$\bar{1}\bar{1}$0)

(01$\bar{1}$0)

Figure 11.   RHEED diffraction patterns from GaN film deposited on Al_2O_3 substrate

most effective in activating the NH_3 as this relatively heavy molecule (17 amu) is accelerated to superthermal velocities in a He (4 amu) stream. This effect could be precluded if a carrier gas that is heavier than NH_3 such as Ar (40 amu) were employed. Therefore, Ar was used as a carrier gas in this series and the orifices were enlarged to permit operation at very close to the same pressures and flow rates as employed for deposition using He. Table IV compares the significant pressures and flow rates employed for deposition using He and Ar carrier gases.

17

Fixed conditions were: TEGa bubbler at -10°C with 40 sccm of carrier, NH₃ nozzle at 550°C, heat sample to 550°C under NH₃ jet, start TEGa flow and hold at 550°C for 5 minutes, ramp to 600°C and grow for 3 hours.

Although it was possible to achieve very comparable NH₃:TEGa ratios whether using Ar or He as a carrier, the total reactant flux possible with Ar at a ratio of ≈350 was 83% of that achievable with He due to the lack of large enough orifices. However this limitation was accepted for the current work in order to develop a baseline and several samples were processed using Ar as a carrier. No dense or transparent films were produces under the conditions examined. Typical films were yellow or black and had a powdery appearance. Figure 12 is an Auger electron spectrum collected from one of the films after 10 minutes of Ar

Table IV. Comparing He and Ar as Carrier Gases

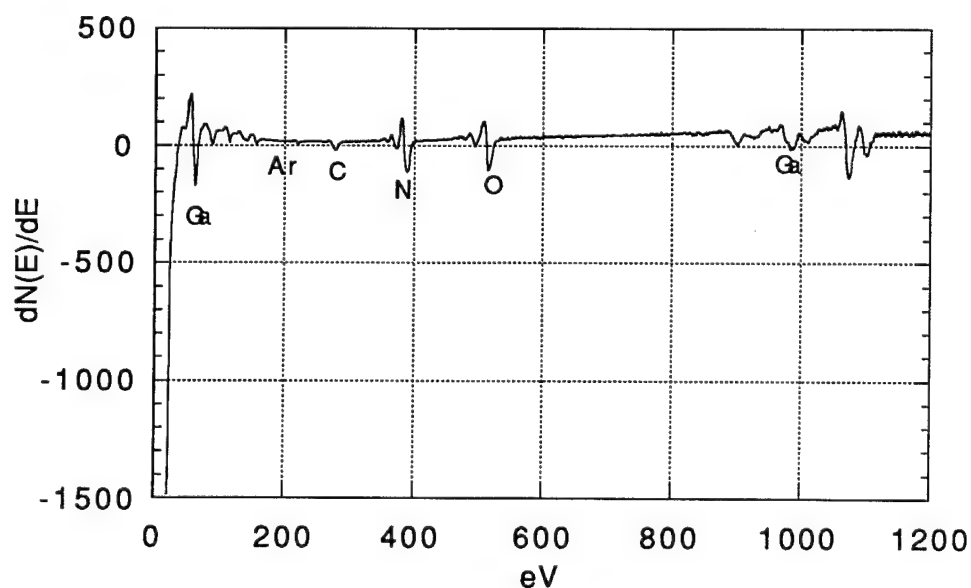| Parameter	He carrier	Ar carrier
TEGa bubbler Press.	860 Torr	1100 Torr
NH₃ jet pressure	800 Torr	1000 Torr
NH₃ flow rate	12 sccm	10 sccm
NH₃:TEGa ratio	354	343
Relative reactant flux	1.0	.83

Figure 12.   Auger electron spectrum of GaN film deposited using Ar as a carrier.

ion milling. As can be seen in the figure, the N:Ga ratio of this film is severely depressed and a large amount of O is present. These observations are consistent with an essentially Ga coated substrate that oxidized during transfer from the supersonic jet reactor to the Auger analysis system. These results indicate that seeding the reactants into He streams significantly enhances the deposition of GaN films.

Assembly of the New SEED and Film Characterization Facility. All of the major components for the new facility have arrived and most have been verified. The specific materials are assigned to the appropriate chamber, only changes from the previous report are detailed:

Source Chamber:

- Chamber completed and leak checked and polished externally, bead blasted internally.
- High speed (400 Hz) motors for beam choppers ordered

Deposition Chamber:

- Deposition chamber has arrived
- Rotatable table for mass spectrometer has arrived
- Elevator for mass spectrometer has been fabricated
- RHEED system has been ordered.

Analysis Chamber:

- Analysis chamber has arrived and has been tested to 1×10^{-10} Torr.
- XPS system has been installed and is being tested.

Transfer Line and Loadlock

- APD cryopump has arrived but has not been tested.
- Gate valves for transfer line have arrived.

D. Future plans

1. Existing deposition chamber to be deactivated and disassembled as the lab space and many components are needed for the new system.
2. Test XPS system, currently underway.
3. Design high temperature nozzle for source chamber.
4. Design manipulator for analysis chamber.

E. References

1. S. Nakamura, Jpn. J. Appl. Phys.**30**, L1708.
2. Z. Sitar, M. J. Paisley, B. Yan and R. F. Davis, Thin Solid Films **200**, 311 (1991).
3. W. J. Meng, J. Heremans and Y. T. Cheng, Inst. Phys. Conf. Ser. **137**, 409 (1993).
4. G. E. McGuire, *Semiconductor Materials and Process Technology Handbook*, Noyes Publications (1988).
5. *Landolt-Bornsteinn* Vol. 17, Springer-Verlag, New York (1982).

IV. Deposition by Dual Colutron Ion Beams

A. Introduction

The goal of this work is to produce crystalline SiC and GaN films by depositing the chemical by two ion beams simultaneously. The ion sources are each equipped with a Wien filter to select the mass of the ions. By using electrostatic deceleration lenses, the ion energy can be selected in the 10 eV range with an energy spread as low as 0.1 eV.

The growth process is monitored during the ion deposition by a reflection high-energy electron diffraction (RHEED) system. A retarding field analyzer is used to examine the structure and composition of the deposited films *in situ* by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). By using the electrostatic ion energy analyzer, low-energy ion scattering spectroscopy (ISS) can be used to characterize the composition of the outermost atomic layer, as well as the structure of the films.

B. Experimental Procedure

Since the last report (September, 1995), the main vacuum chamber has been installed with the electrostatic analyzer, the deceleration lenses, beam deflection units, RHEED system and vacuum pumps in place. The two Colutron ion guns have been assembled and leak-tested. The loadlock chamber and the LEED/AES chamber have been mounted and aligned with the main chamber on the support structure. The sample manipulator has been fitted with the necessary wiring for sample heating and sample current measurement. A Faraday cup for ion current density measurement and beam profile analysis has been mounted on the sample holder. The construction of the gas manifold for Colutron ion source 1 is under way, see Fig. 1. The electronic interface between computer and power supplies for the electrostatic energy analyzer is under construction.

C. Results

The assembly of the experiment is almost complete. Parts of the setup have been leak-tested.

D. Future Research Plans and Goals

After the completion of the dual ion-beam deposition system, the ion sources will be tested and the ion beams will be characterized. The LEED and AES data acquisition system will be assembled. After the successful test of the equipment, SiC films will be deposited. Analysis of these films will be performed *in situ* by RHEED, LEED and AES and *ex situ* by RBS and LEEM. In the next step, the deposition of GaN films on SiC substrates is planned.
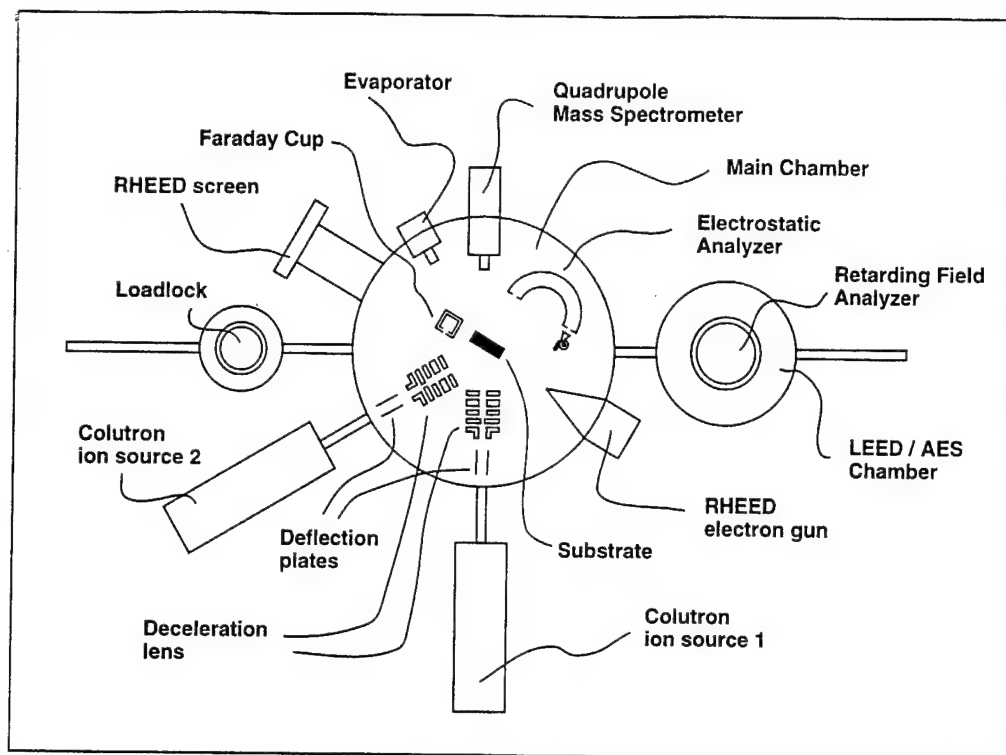
Figure 1.   Schematic drawing of the dual Colutron ion beam deposition experiment. The setup consists of a loadlock, the main chamber connected to the two Colutron ion sources and a LEED/AES chamber.

V. Testing of a NH₃ Seeded He Supersonic Molecular Beam Source for *In Situ* Growth of AlN and GaN Layers Observed by Low Energy Electron Microscopy (LEEM)

A. Introduction

The nitride family of AlN, GaN and InN thin films have shown to be strong candidates for electronic and optoelectronic applications. With direct band gaps of 6.2 eV, 3.4 eV and 1.9 eV for AlN, GaN and InN respectively, solid solutions based on these materials provide for band gap modifications suitable for applications ranging from the red to the deep UV region of the spectrum [1]. However, the growth of single-crystalline epitaxial films with low defect densities has proven to be troublesome. As-deposited GaN shows n-type behavior which has been proposed to be due to N vacancies [2]. These vacancies are formed during growth due to the high temperature required to decompose N sources such as NH₃ and to obtain high enough surface mobilities to form a single-crystalline film. Other N sources such as cold cathode ion guns [3] and microwave discharges [4,5] have been used to dissociate N_2 and N_2/NH₃ mixtures respectively to promote low temperature (i.e. 650°C) growth of GaN. However, it has been shown that high-temperature anneals would improve the carrier density and crystallinity of the films [6]. Therefore, a technique which would provide a reactive N source with a low decomposition temperature and high surface mobility would be desirable in order to overcome these difficulties.

Supersonic molecular beam epitaxy (SMBE) has been shown to enhance the surface decomposition of silane and methane [7,8]. This is due to the possibility of tuning the kinetic energy of these species such that bond cleavage and deformation occurs upon contact with the substrate. If the kinetic energy available is higher than the barrier for chemisorption on these surfaces, some of the remaining energy can be used to enhance surface diffusion either directly by the adsorbate or indirectly via the generation of surface phonons. Supersonic molecular beam epitaxy also provides for the tuning of the energy spreads. This is important in order to experimentally determine the chemisorption barriers for the systems being studied, as well as to provide species with high sticking coefficients at high enough intensities. Supersonic molecular beam epitaxy is, therefore, a useful technique for the growth of single-crystalline GaN films at suitable growth rates. A review of supersonic molecular beams can be found in Scoles [9].

The present report entails preliminary results on the characterization of NH₃ seeded He supersonic molecular beams. Modifications to the gas manifold described previously (Progress Report from October 1995) are presented.

B. Experimental Procedure

A 10% NH₃/90%He mixture was compressed to 25 ktorr and expanded into the helium atom scattering chamber through a 25 μm diameter nozzle to yield a supersonic molecular

beam. The base pressure of the system was 10^{-4} torr. The beam was extracted by a 0.5 mm skimmer and chopped using a rotating disk chopper (Boston Gear, model E15). The beam was differentially pumped to a pressure of 10^{-9} torr in the detector chamber for time of flight (TOF) analysis. The TOF spectrum was measured with a quadrupole mass spectrometer synchronized with the chopper aperture.

A 500 cm^3 reservoir has been designed for use with the current gas handling manifold. The NH$_3$/He mixture will be pressurized to 1600 psi into the reservoir. The reservoir will serve as the source gas which will be used for deposition by regulating the delivery pressure. The delivery pressure will be kept under 1000 psi. This addition will provide for a greater nozzle pressure stability and reduction of vibration by the compressor during deposition in the LEEM. The volume was chosen such that deposition times of 60 min can be attained with the compressor turned off.

C. Results and Discussion

Figure 1 shows the energy spectra at 300K and a value of P_oD (nozzle pressure-diameter product) of 63 torr-cm for pure He and a 10% NH$_3$/He mixture. The mean energy for pure He
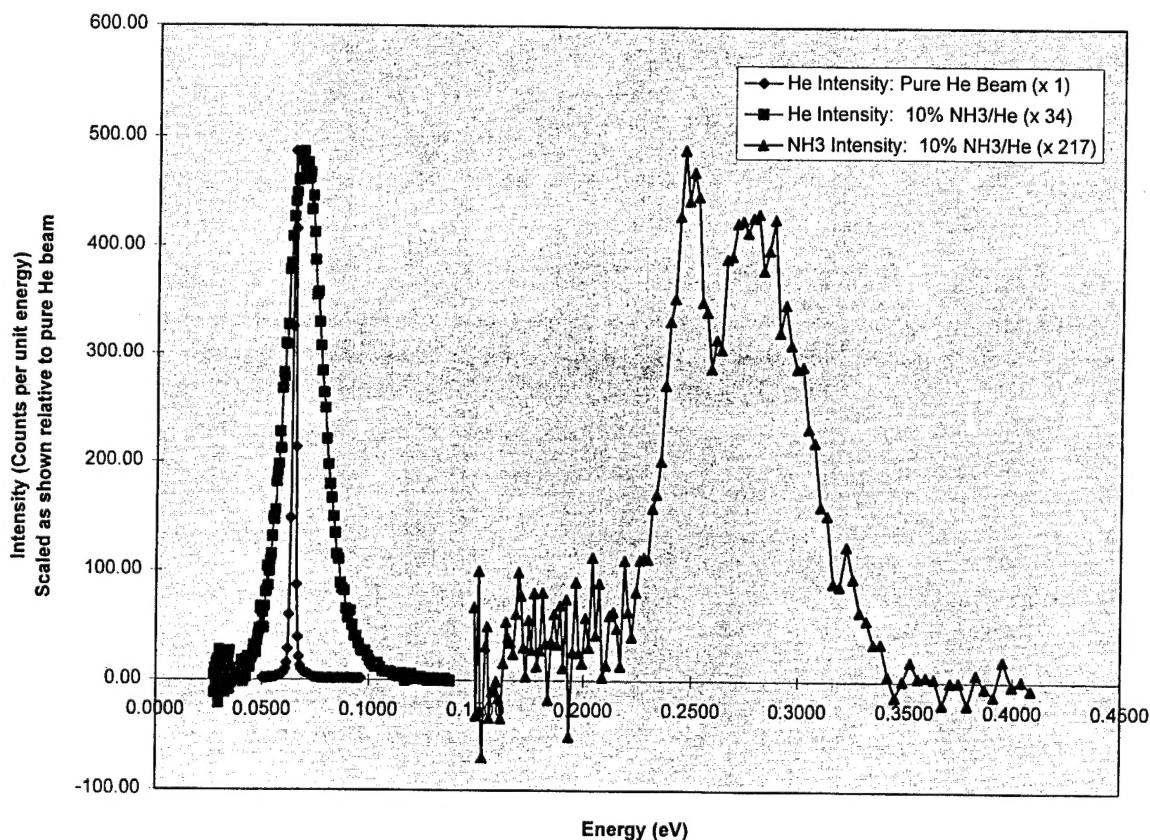

Figure 1.   Seeded beam energy distributions. 10% ammonia seeded into helium.

is 0.064 eV with an energy spread of 0.002 eV. Upon mixing with 10% NH_3, the mean energy increased to 0.070 eV with an energy spread of 0.022 eV. This result is surprising since for an ideal gas, the presence of a heavier species should slow the lighter component of the mixture. Real gas enthalpy effects may be quite important, however, an effect which is easily investigated by measuring the terminal beam velocity at different source pressures. The NH_3 molecules have a mean energy of 0.264 eV with an energy spread of 0.068 eV. This is also surprising since the energy calculated for this mixture for a source with infinite mach number is 0.205 eV. There appears to be two peaks in the energy distribution, one at 0.308 and another at 0.24 eV. It is possible that $(NH_3)_x$ (x=2,3,4....) clusters nucleate during the expansion of the gas. Release of the latent heat of condensation into the beam could explain the higher-than-expected beam energies. Differential aerodynamic acceleration of monomers and dimers could give rise to the twin peak structure in the NH_3 energy distribution. These effects will be investigated experimentally in the next few months.

D. Conclusion

Preliminary results indicate that NH_3 seeded supersonic molecular beams produce highly accelerated NH_3 molecules with velocities approaching that of pure He at an infinite Mach number. However, further studies are required to examine and interpret the energy spectra at different temperatures.

F. Future Work

The characterization of NH_3 seeded supersonic molecular beams will be completed. A $500 \ cm^3$ reservoir will be installed into the gas manifold to increase the pressure stability of the system and decrease vibrational effects from the compressor during deposition in the LEEM. Testing of the source chamber and preliminary film growth will be performed.

G. References

1. S. Strite and H. Morkoc, J. Vac. Sci. Technol. **B10**, 1237 (1992).
2. A. Estes Wickenden, D. K. Wickenden, T. J. Kistenmacher, J. Appl. Phys. **75**, 5367 (1994).
3. Z. Q. He, X. M. Ding, X. Y. Hou, Xun Wang, Appl. Phys. Lett. **64**, 315 (1994).
4. M. J. Paisley, Z. Sitar, J. B. Posthill, R. F. Davis, J. Vac. Sci. Technol. **A7**, 701, (1989).
5. H. Okumura, S. Misawa, T. Okahisa, S. Yoshida, J. Cryst. Growth **136**, 361 (1994).
6. D. K. Wickenden, J. A. Miragliotta, W. A. Bryden, T. J. Kistenmacher, J. Appl. Phys. **75**, 7585, 1 June 1994.
7. M. E. Jones, L. Q. Xia, N. Maity, J. R. Engstrom, Chem. Phys. Lett. **229**, 401 (1994).
8. S. T. Ceyer, J. D. Beckerle, M. B. Lee, S. L. Tang, Q. Y. Yang, M. A. Hines, J. Vac. Sci. Technol. **A5**, 501 (1987).
9. D. R. Miller, *Atomic and Molecular Beam Methods*, Ch. 2, Ed. G. Scoles (1988, Oxford University Press).

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